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Development of a Process for Conversion of Wood into Liquid Fuel

by

D.G.B. Boocock and D. Mackay

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ENFOR Project C-44

Development of a Process for Conversion of Wood into Liquid Fuel

by

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December 1982

TABLE OF CONTENTS

	Page
ABSTRACT	i
PREAMBLE	1
PERSONNEL	1
INTRODUCTION	2
LABORATORY SCALE CONTINUOUS/SEMI-CONTINUOUS UNIT	4
Schematic Diagram	5
Photograph of Reactor	6
Photograph of Control Panel	7
Photograph of Slurry Tank	8
Mode of Operation	10
Charging	10
Product Collection	12
Progress of Construction and Operation	13
Proposed Timetable	14

Assessment of Operation 15

Photograph of Feed Adapter 17

Suggested Modifications 18

FAST HEAT-UP STUDIES 20

Introduction 20

Experimental 23

Apparatus 23

Technique 24

Diagram of unit 25

Results and Discussions 28

Effect of residence time 29

Comparison of catalytic and non-catalytic runs 31

Graphs of results 32

Hydrogen/carbon atomic ratios in oils 33

Conclusions and Continuing Studies 33

References 35

Tables 37

ABSTRACT

A laboratory scale continuous/semi-continuous wood liquefaction unit has been constructed and partially evaluated. The unit consists of 2-L stirred tank (high pressure) reactor. A slurry of wood in water is fed to the reactor through a tubular lock system. High pressure water displaces the slurry into the reeactor. The water is then backflushed from the lock with more slurry. Product discharge is via a dip tube to another cooled lock system from where it is discharged to a separation vessel. At the present time hydrogen is supplied to the reactor from high pressure (4000 psi) cylinders.

The four valves controlling the feed system and the two valves controlling the discharge are remotely operated using air operated drives. A control panel is located about 6 metres from the reactor. A recycle system prevents the slurry from settling before feeding to the lock.

The unit has been operated with 30 mesh and 100 mesh wood. Plugging at the reactor inlet occurs with 30 mesh wood, but liquefaction is accomplished with 100 mesh wood. Under a new one year ENFOR contract the unit is being modified to overcome the plugging problem.

At the same time research has proceeded on the conversion of wood to oil by rapid pyrolysis of wood in water. Although not funded directly by the ENFOR contract, the results are very relevant to the future of the wood liquefaction unit. Poplar wood, when heated rapidly (70-90 s) in water to 350°C and quenched, yields oil in 55 per cent mass yield. Approximately 75 per cent of the wood carbon and hydrogen is retained in the oil. The oil contains 25 per cent oxygen (wood contains 45 per cent). Extended reaction significantly lowers yields which are the same in the presence of both nitrogen and hydrogen atmospheres. Nickel carbonate addition lowers yields significantly. Experiments have been limited to wood particles less than 35 mesh (0.73 mm grid) but heat transfer studies are being extended to larger particles.

PREAMBLE

The work carried out under the contract relates specifically to the construction and operation of a laboratory-scale continuous/semi-continuous wood liquefaction unit. However, the total wood liquefaction program has included two other major areas:

1. Batch autoclave work, used to identify general features of the liquefaction process.
2. The construction and operation of a small-scale fast heat-up wood-liquefaction unit.

This report contains results from area 2, since these are relevant to the further assessment of the operation of the constructed unit.

PERSONNEL

Mr. Hector Franco (M.A.Sc., University of Toronto) was involved in the early phases of the design work. He drew up the preliminary design and was responsible for ordering the major components for construction of the continuous unit. When Mr. Franco left, his place was taken by Mr. Allan Jenkins, another M.A.Sc. graduate of this Department. Mr. Jenkins has great strengths in the area of design and construction, and simultaneously he commenced construction of the unit and modified its design. In 1981, Mr. David Beckman, also a Master's graduate of this

Department, worked with Mr. Jenkins in bringing the total facility to an operable state. Mr. Beckman took over the total operation when Mr. Jenkins left to become a manager of the biomass program in the province of Manitoba. Mr. Beckman made the final tests (up to April 1982) on the facility which led to the reassessment of the unit and identification of necessary modifications.

Mr. Peter Lee, who was an M.A.Sc. student in this Department, also assisted with some phases of the project.

We would like to thank Dr. R. Overend, the Scientific Authority on this contract, for his very valuable comments, suggestions and guidance.

INTRODUCTION

The major objective of the work performed under the contract, was to take the existing knowledge on catalytic wood liquefaction, and design and construct a small-scale (ca 2 L capacity) continuous system capable of wood conversion at a rate of 0.2 kg/h. Our own extensive work, using batch autoclaves, made up a large part of the prior knowledge. The system was to be tested using prolonged continuous runs, thus generating data essential for the design of larger scale pilot plants.

The key to the design of the system was the problem of feeding, from atmospheric pressure, a wood/water slurry to a system containing a pressure equivalent to the vapour pressure of water at 350°C plus

pressures due to added or generated gases. A similar problem existed for removing product from the reactor. A secondary consideration was the rate of feed which would be necessary to satisfy the optimum residence time of the wood. This latter parameter was not available. All data at the start of this project, had been obtained in batch autoclaves in which heat-up times to 350°C were usually no less than one hour, and thus the rate of liquefaction when wood was very quickly heated to 350°C was unknown. If the optimum residence time were very short, then the addition of fresh, cold feed would place a large thermal load on the reactor, even if the feed were preheated to some extent. In the absence of this important information, it was decided that the reactor itself would be a 2-L vessel of the same type used in our batch runs. The system would be designed to supply feed and discharge product, while the autoclave was operating. A choice had to be made on the type of feed system. A truly continuous system might consist of a screw feeder, the rate of feed being controlled by the rotation of the screw. However, at the start of the project, this type of feed system was still not fully evaluated, and we were hesitant to adopt it. We desired a proved system which would be reasonably reliable in delivering a wood/water slurry into the reactor operating at temperature. We thus opted for a lock system, thus sacrificing some element of continuity for the sake of reliability.

In this lock system, slurry in the lock would be displaced downwardly by water and into the reactor. After the slurry had cleared the lock, the water would be upwardly displaced by more slurry. The

volume of the lock, the rate of feed from the lock and the number of feed cycles would together control the thermal load on the reactor. It was anticipated that the lock would be sufficiently large that a slow feed rate would be normal, and cycles would be infrequent. This, coupled with rapid lock recharging, would produce an operation barely distinguishable from a truly continuous function. We would also have the capability of rapidly charging relatively large volumes of feed to an autoclave, thus increasing the versatility of the system. A similar system, but using a second autoclave rather than a lock, was used by Osterman for kinetic studies on cellulose liquefaction (this unit was not continuous). A lock system was also chosen for the product let-down and collection system.

LABORATORY SCALE CONTINUOUS/SEMI-CONTINUOUS UNIT

A schematic diagram of the unit as it existed as of April 1982 is shown in Figure 1, and photographs are included in the main copy of this report for reference.

The unit is based on a 2-L Autoclave Engineering (AE) packless Magnedrive-stirred autoclave. The only modification ordered was the

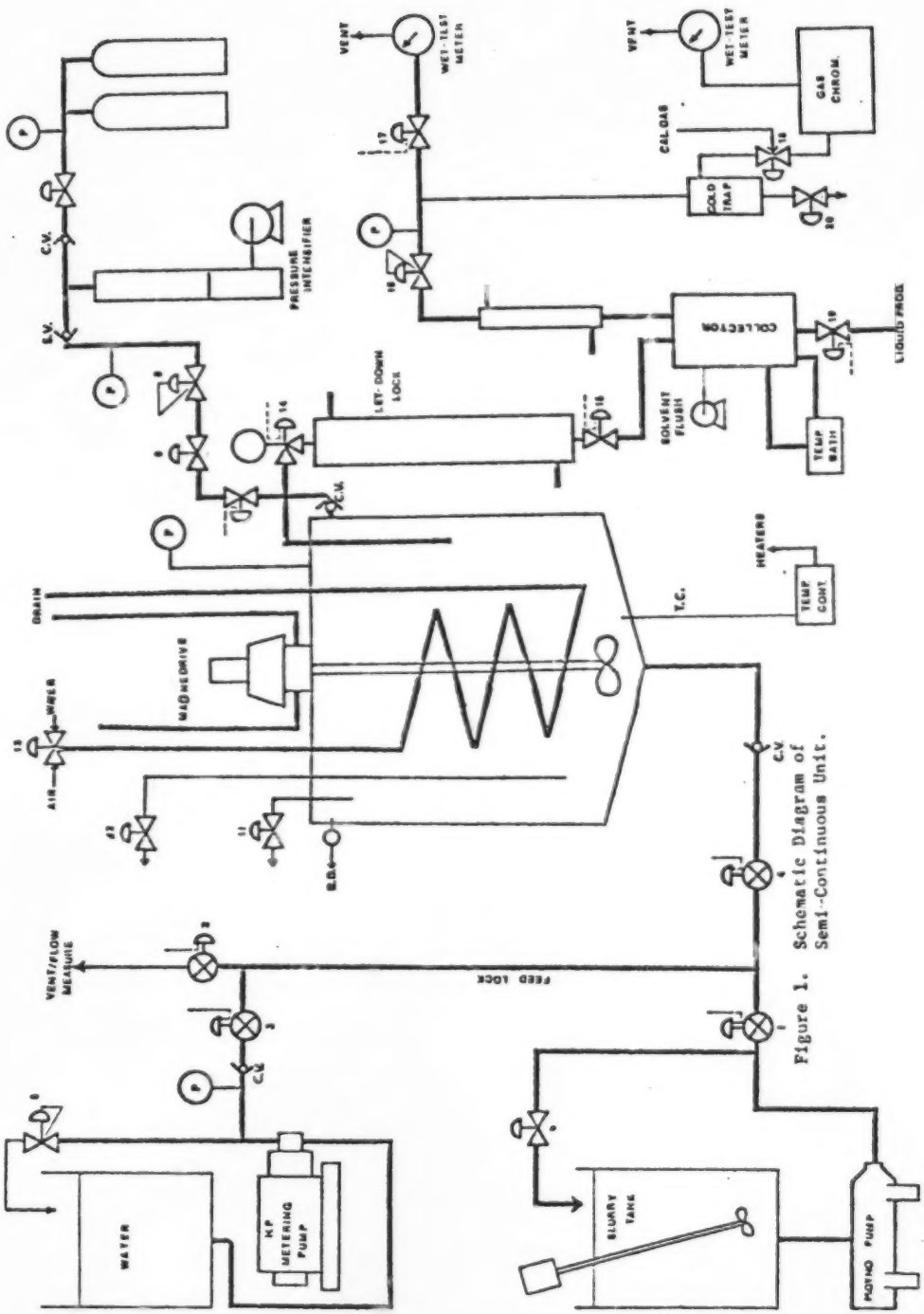
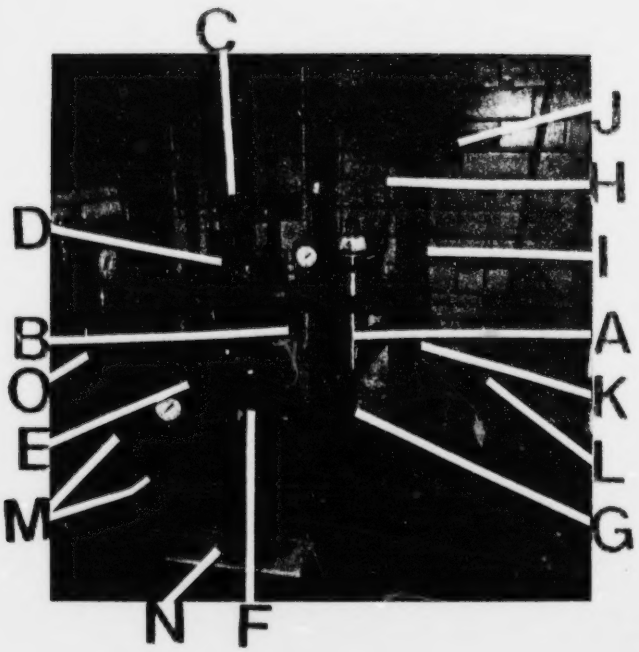
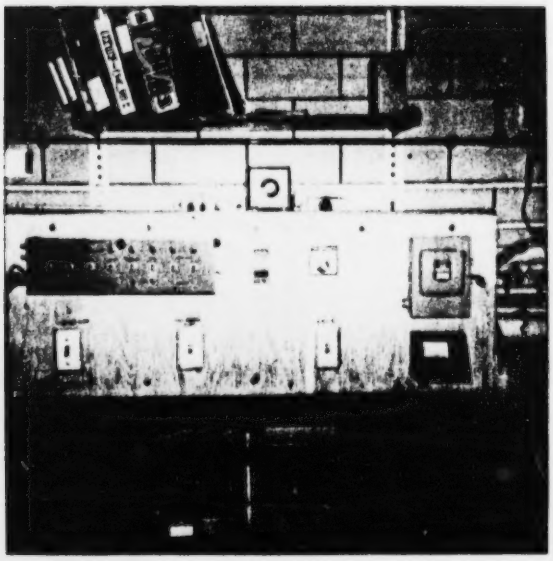


Figure 1. Schematic Diagram of Semi-Continuous Unit.



This photograph shows the 2-L reactor vessel, A (silver) with magnedrive clearly visible on top. The cylindrical heater, B has been removed and is stored horizontally to the left of the reactor. The four air-operated controllers (red) can be clearly seen. The upper one, C, controls the lock vent. The next controller down, D (in vertical position) controls the high pressure water feed (the vertical lock itself is hidden by this controller). The next controller, E (horizontal across the photograph) controls the slurry feed line and the bottom controller, F operates the valve for the feed to the reactor. The feed line, G (black) runs horizontally under the frame, bends upwards and enters the base of the reactor. The product leaves the reactor via the silver tube, H (parallel and slightly to left of right vertical frame member (blue)) and enters the cooled lock, I (2/3 black, 1/3 copper colour) vertical and to right of the same member. The controllers and valves J, K (blue) can be clearly seen on each end of the lock. The collection vessel is mounted on a Dexian frame in the bottom right hand corner of the photograph.

The slurry recycle pipes, M can be seen at lower left. The high pressure water pump, N is located in the foreground and the feed line from it, O (silver) runs parallel to the left edge of the photograph, bends through a right angle (note large pressure gauge), and continues to the lock.



This photograph shows the control panel which is located about 6 metres from the reactor. The 8 switches (grey box-upper left) operate (from left to right) the 4 controllers for the valves around the feed lock, (i.e., lock vent, inlet from low pressure slurry, inlet from high pressure water system, and inlet to the reactor), product lock inlet and outlet, and gas vent and liquid vent from the collection vessel. The 3 identical switches on the bottom are the main switches for (from left to right) the Moyno pump for the slurry circulation system, the high pressure water pump and the magnedrive stirrer. The meter with black surround (bottom right) measures the rpm of the stirrer. The heater mains shut off is located top right. To the left of this is the temperature controller. Located on top of the control panel is a 6 position switch box which together with a digital readout (to be installed) will allow measurement of temperature at 6 locations in the equipment.

This photograph shows the slurry tanks; the discharge tank (or second slurry tank) is on the left and the feed tank on the right. The tank for the high pressure water is not shown but is to the left of the photograph. The Moyno pump for the slurry recycle is shown below. The return lines to both tanks can be seen in the upper part of the photograph.

facility for a bottom feed. We considered that the head ot the autoclave was too crowded to accommodate a feed line of sufficient diameter.

The lock itself is a piece of AE high pressure tubing (internal diameter 1.3 cm) rated at 30 MPa (4500 psi max) and having a volume of about 130 mL. The original intention was to place sight glasses at either end to visually observe the discharging and recharging of the system. However, the pressure specifications on available sight glasses made their use dubious from the safety aspect, and thus it was decided that the valve timings for charge and discharge would have to be determined by experimentation. Ultra-sound and radioactive detectors for wood/water systems have been investigated, but no suitable detector has yet been found. The lock system is controlled by four Mark ½" stainless steel ball valves. Originally these were to be manually operated, but since the opening and closing of these valves is critical, particularly the sequencing, it was decided, in consultation with Dr. Overend, that these valves should be remotely operated through Marpac air operated drivers. The valves are normally closed and are opened by the drivers. Failure of the air pressure results in closure of the valves. The valves are operated by switches on the remote panel but are wired so that the contents of the autoclave cannot accidentally be discharged to the atmosphere. The catalytic process uses a hydrogen atmosphere and the original intention was to provide high pressure hydrogen using an available gear pump and high pressure reservoir and not purchase a

hydrogen compressor at this time. However, it was believed that the gear pump would be unable to supply sufficient hydrogen. Fortunately a temporary solution has been found. High pressure hydrogen cylinders, as supplied to us, contain 26.7 MPa (4000 psi) compared to the expected 23.3 MPa (3500 psi). Thus we have been skimming these cylinders, and this will continue until the system is truly proved, at which time it will be decided if a more advanced system is required.

The slurry feed system consists of a stirred slurry tank from which slurry is fed to a plastic recycle line which leaves the base of the tank, passes to and from the reactor and then discharges into the top of the slurry tank. The slurry feed is tapped from the recycle line. The height of the discharge line back into the tank helps control the filling of the lock in that the slurry rises in the lock, passes beyond the top valve and is prevented from rising further, since it is now at the same height as the discharge line. This prevents excessive discharge of slurry to waste.

MODE OF OPERATION OF UNIT

1. Charging

A filling sequence for the continuous unit consists of the following (it is assumed that the autoclave is at a temperature of 350°C):

(a) With the slurry in the tank stirring, and the slurry recycle line in operation, driven by a Robbins and Myers Moyno pump, the lock is filled by opening valves 1 and 2 (see schematic diagram). The slurry passes beyond valve 2 where it stops, due to the limit in pressure head controlled by the discharge return to the slurry tank. Because of the surge, a small amount goes to waste together with the water which is displaced from the lock.

(b) The low pressure filling and vent valves (1 and 2) are closed, and a high pressure hydraulic (water) line valve (3) is opened. Hydraulic pressure is generated using a Milton-Roy Milroyal Model A metering pump. Pressure in the lock system is controlled by a Tescom back pressure regulator. On the condition that lock pressure is higher than the reactor pressure, the reactor inlet valve (4) is opened, and the feed hydraulically pumped into the reactor. High pressure feed rate is controlled and measured using a stroke length adjuster and electronic stroke counter on the metering pump.

(c) When the lock has nearly emptied, the reactor inlet valve is closed, and the vent valve opened to bring the lock to atmospheric pressure ready for the next cycle.

(d) Hydrogen gas is fed to the reactor headspace from cylinders through a Tescom high pressure regulator and check and surge valves.

Towards the end of the contract, the slurry recycle loop was provided with a water flush system. This was necessary because the slurry

in the recycle line settled when recycling was terminated, and this led to blocking of the recycle loop.

Clearances have been left for the incorporation of preheaters. The feed line has a cooling jacket which could also be used in a heating capacity.

2. Product Collection

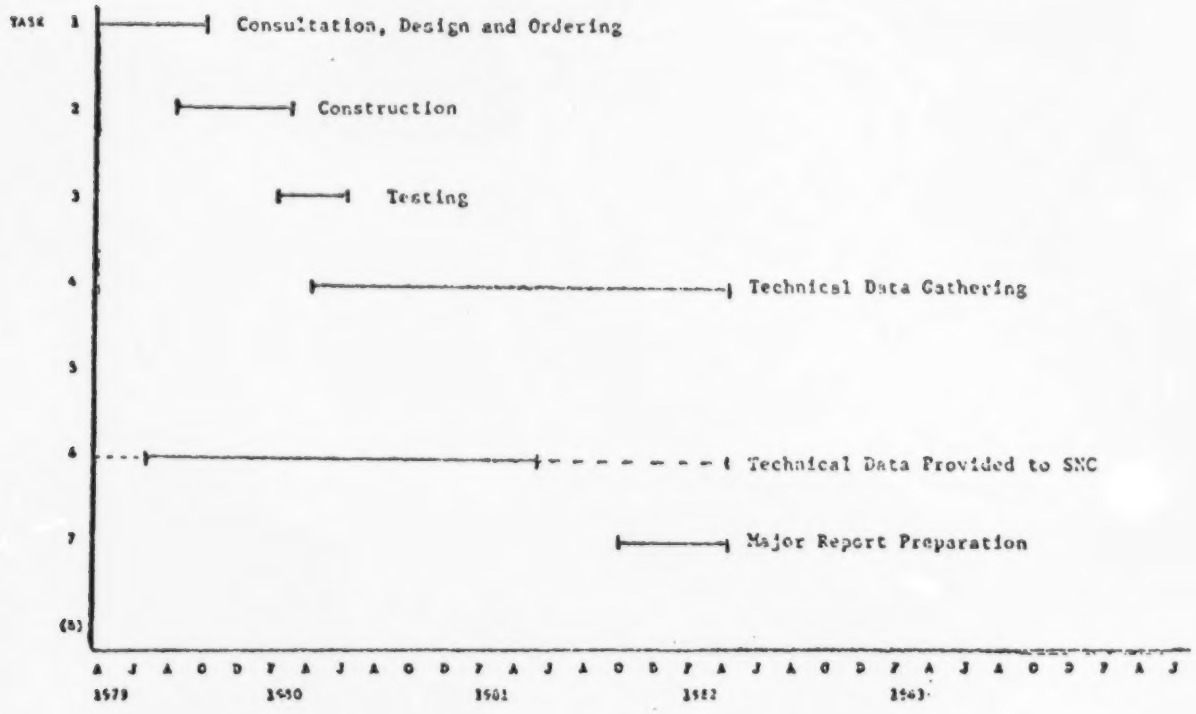
Hot product leaves the reactor via a 3/8" dip tube. Entry into a primary let down lock is controlled by a remotely air operated Autoclave Engineering 3/8" medium pressure valve. The lock consists of 1" Autoclave Engineering tubing and fittings which are cooled by water flowing through an external copper jacket. Pressure and temperature in the lock are monitored. Exit from the lock is controlled by a valve, similar to the lock inlet valve, and can be controlled manually or (as planned) automatically by a pressure switch. Product (liquid and gases) flow to a separation vessel. Gas is vented through a regulator and volume measured using a wet-test meter. Gas analysis of a pilot flow sample is performed automatically by a Hewlett Packard HP 5880A with a dual column system and thermal conductivity detectors. Liquid is collected from the bottom of the separation vessel and can be further processed by centrifugation and distillation. Solvent flush can be used for periodic removal of residuals from the collection vessel.

PROGRESS OF CONSTRUCTION AND OPERATION

The original timetable (attached) anticipated construction of the unit in a useable form would be complete by April 1980; i.e., one year after the start of the contract. Even under ideal circumstances, this date for completion would have been unrealistic. The initial design led to a major ordering phase with the usual time lag for delivery. Inevitably, some incorrect items were sent and had to be reordered with again the usual delay (6 weeks quoted, but longer in practice). The unit was then constructed in a bare bones form. After consultation with Dr. Overend, some design changes, relating mainly to safety features, were recommended. The lock valves and let down valves, which were originally manual in operation, were equipped with air operated drivers. The control switches for these drivers and the electronics for the unit were removed to a more remote location between the unit and the exit door of the facility. At a later date, necessary modifications such as the slurry recycle line and the water flush system were constructed. These necessary delays did not prove critical since SNC did not require the technical data that we had anticipated in the proposed timetable. In fact this development proved somewhat advantageous in that it allowed us to bring the apparatus to an improved state of sophistication, and more importantly, it allowed a greater degree of hazard assessment and the incorporation of more safety features. The unit was thus ready for testing by January, 1982.

TIMETABLE:

Proposed Timetable

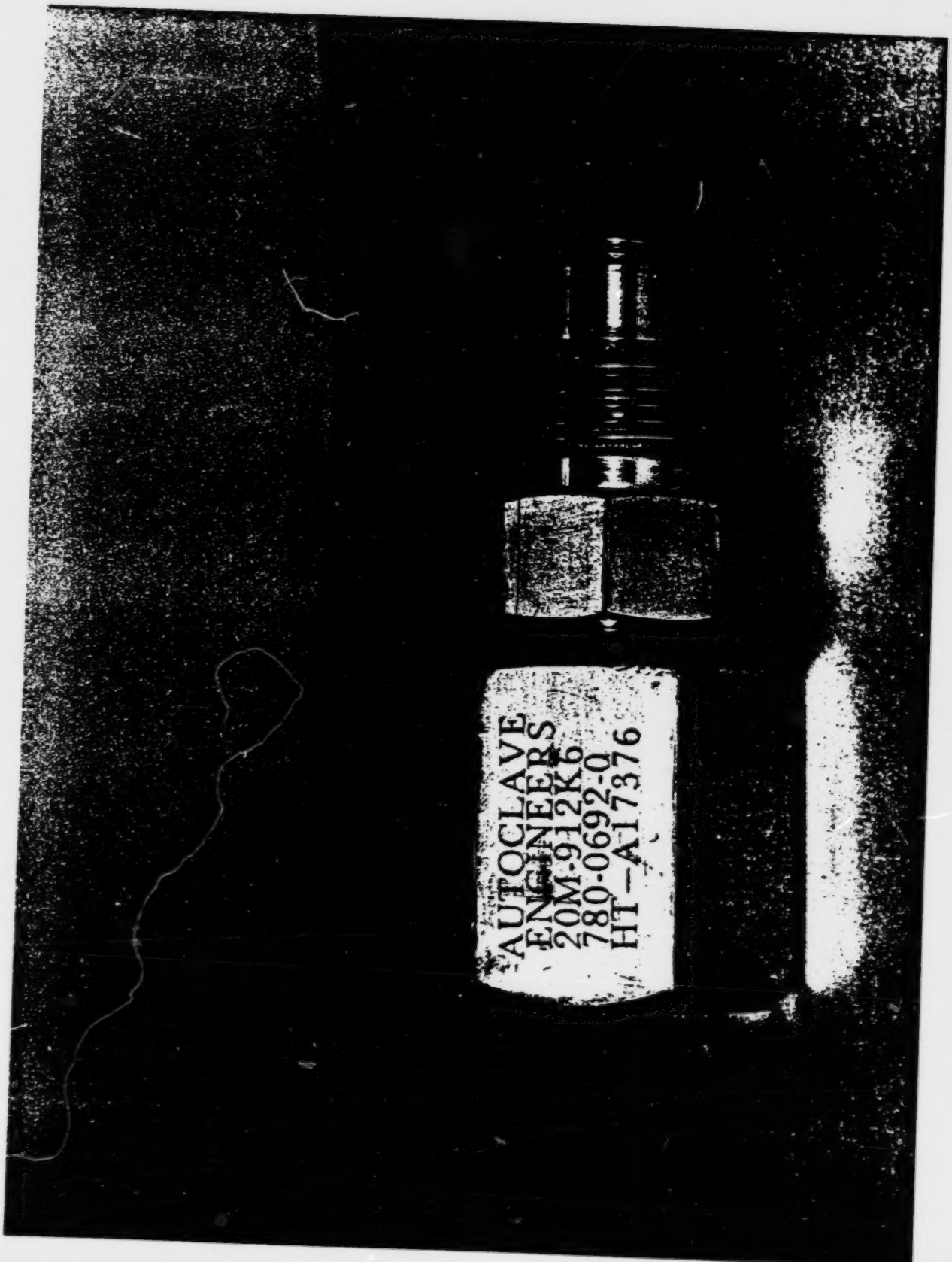


ASSESSMENT OF OPERATION OF UNIT

The unit was first tested at atmospheric pressure replacing the lock with a transparent plastic tube. This was done to determine approximate time delays for valve sequencing. A slurry of wood in water (30 mesh wood, 8-10 wt%) was used. Plugging of slurry occurred at the inlet valve and at the base of the reactor where the feed line entered the autoclave. The former plugging was caused by a restriction in the nipple to valve adapter. The plugging at the reactor inlet proved more serious and was due to the reduction in the feed line diameter in the adapter: The internal diameter of the feed line is 1.3 cm (0.516") whereas the exit orifice of the adapter was 0.8 cm (0.312"). As a result of these observations the regular lock system was installed and the system tested with the head of the autoclave removed, i.e., charging feed against essentially atmospheric pressure. Plugging at the inlet valve did not appear to occur but again plugging occurred at the reactor inlet. The unit was also tested with a pressure differential of 23.3 MPa (4000 psi) but the plug remained intact. The inlet fitting is shown in the attached photograph. Wood of less than 60 mesh did not appear to plug and thus in the short time available some protracted runs were performed to determine if wood would be liquefied in the unit. Three runs serve to illustrate problems which were encountered and which led to suggested changes in equipment design and operation.

In the first run, a slurry of 8-10% wood (smaller than 60 mesh) was added to the autoclave. A nickel carbonate/wood ratio of 1:5 was used. The autoclave was filled to just below the dip tube exit (1350 mL). The unit was sealed, flushed three times with hydrogen, pressurised to 300 psi and heated to 350°C. The heating step took 70 minutes after which time the pressure was 16.7 mPa (2000 psi). Two portions (2 x 130 mL) of feed were added from the lock at 20 minutes and 40 minutes after heat up respectively. (It took approximately 20 minutes for the autoclave to return to 350°C after feed addition.) After 40 minutes the pressure was raised 8 MPa (120 psi) by adding hydrogen, confirming that hydrogen could be fed under operating conditions. Two occurrences led to termination of this run. First, thermal shock caused leakage at the inlet fitting of the autoclave and bursts of steam were noted. Secondly, there were problems in the magnedrive caused by vapours leaking through the seals. Wood liquefaction occurred but most of the wood was in the reactor initially so this was not surprising. However, no unreacted wood could be seen in the product mixture. A second run showed similar problems and was similarly terminated.

In the third run the feed was preheated by circulating hot water (60-65°C) through the coil surrounding the feed line. This served two purposes. First it reduced the thermal shock at the inlet fitting and secondly it allowed a shorter time between feeding cycles. The autoclave was charged as before with the slurry (8-10%) of < 60 mesh wood in water (1350 mL). The autoclave was flushed three times with hydrogen and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heated to 350°C (70 minute). After a further 3 minutes the first lock feed was added. The reactor returned to temperature approximately 8 minutes after the addition compared to 20 minutes when the feed was not preheated. A second feed portion was added 2 minutes after the autoclave had returned to 350°C.

By this time the pressure had risen to 24 MPa (3600 psi) as a result of the head space reduction. The product lock was therefore filled and let down resulting in a drop in the autoclave pressure to 20.7 MPa (3100 psi) followed by a slow increase. A third feed portion was added 13 minutes after the second and this resulted in a pressure rise to 26.7 MPa (4000 psi). The pressure continued to increase and before the product lock could be used the rupture disc fractured.

SUGGESTED MODIFICATIONS

As a result of the various tests, 2 modifications are suggested for the autoclave. The most important relates to the plugging problem at the base of the reactor. As noted earlier the plugging is caused by a diminution in the feed line diameter as it passes through the adapter to the autoclave. We have ascertained that the hole in the autoclave base can be opened up to 1 inch (H-1 hole) and with a simple fitting the feed line will not have a constriction. This work will have to be performed

by Autoclave Engineering to ensure that the Autoclave still meets its specifications.

A second modification is suggested by the test in which large pressure changes where observed when the feed was added. The same modification was also suggested by our results from our rapid hydropyrolysis studies . At the present time the dip tube inlet is about 4 inches below the head of the autoclave, the autoclave itself having a depth of 13 inches. The autoclave has to be reasonably full before product can be discharged through it. The volume of the lock is thus significant compared to the head space in the reactor and thus addition of feed (and removal of product) caused fairly large pressure changes in the autoclave. Because of this, and in anticipation that shorter residence times will become normal, it is recommended that the dip tube be extended to near the base of the autoclave. An ENFOR contract for one year has already been awarded under which the modification will be made and the equipment evaluated further.

It is possible that the unit may eventually be used for rapid hydropyrolysis in which residence time may well be determined by thermal limitations. Since hydrogen is not required for the hydropyrolysis the decision regarding the acquisition of a hydrogen compressor should be delayed.

FAST HEAT-UP STUDIES

INTRODUCTION

In response to the dramatic events of the 1970's, considerable research has been done on the biochemical and thermal conversion of biomass to liquid fuels and chemicals. Liquefaction by catalytic hydropyrolysis has received considerable attention over the past few years, and two types of process have been studied in some detail. Several groups have studied the treatment of wood and other substrates, such as peat, with aqueous sodium carbonate and carbon monoxide mostly at temperatures around 350°C (Appell et al, 1970, 1971, 1975; Eager et al 1982; Elliott 1980; Osterman et al 1980; Bjornbom et al 1981). Studies on cellulose at 250°C show that carbon monoxide increases the rate of liquefaction (Osterman et al 1980). In the other type of catalytic hydropyrolysis, nickel metal and hydrogen are used to liquefy wood at 350°C (Boocock et al 1979a, 1979b, 1980a, 1980b). Similar catalytic pyrolyses of cellulosics have also been studied at somewhat higher temperatures in mineral oil slurries (Weiss et al 1976). Unlike coal liquefaction, the incorporation of hydrogen into the liquid product is not theoretically required, the hydrogen/carbon ratio of wood being more than sufficient to satisfy the required ratio in the products (Boocock et al 1980b). The major function of the hydrogen is to prevent the nickel metal being oxidised to nickel ions, but unavoidably some

hydrogen is consumed during the reaction. The nickel metal probably helps stabilise the liquid products and prevents charring.

These two types of catalytic reaction have been studied, for the most part, in autoclaves using long heat-up times, the cellulosic study of Osterman et al, 1980, being an exception. Under slow heat-up, non-catalytic hydropyrolysis of wood produces char, probably reflecting a closer approach to equilibrium conditions. Antal (1978) has made equilibrium calculations for cellulose/water mixtures by minimising Gibbs free energy, subject to mass balance constaints. At lower temperatures (300-400°C) the formation of carbon dioxide, methane and carbon is predicted and at higher temperatures (> 500°C) carbon dioxide, carbon monoxide hydrogen and smaller quantities of methane are the predominant species. In wood liquefaction, any oxygen removed should ideally be in the form of carbon dioxide, and not carbon monoxide. Also, methane is an undesirable product, since it lowers the hydrogen/carbon ratio in the substrate and encourages char formation, as does the formation of water. Thus it would appear that the lower temperature range would be more desirable. The lower temperatures would also favour non-equilibrium products, such as volatile liquids, if the temperature increase is rapid. Antal also showed that the actual formation of methane from cellulose/steam mixtures at 500°C is very small, and intuitively one expects some kinetic problems with methane formation. In our own catalytic liquefaction studies (Boocock et al, 1983) a very active form of nickel was required to produce significant amounts of methane. Thus

under rapid heat-up, to a temperature of 340°C, undesirable methane production should not be a problem. If the primary objective is the liquefaction of the wood and not deoxygenation, then rapid heating, followed by quenching maybe suitable, so long as liquefaction proceeds faster than dehydration. Roy et al (1982) have shown that rapid heat-up processes of a non-catalytic type are desirable for several reasons. First, separation of catalyst from product would be unnecessary. Secondly, a gas, such as hydrogen and/or carbon monoxide, would not be required, and finally, a rapid conversion process would imply a smaller plant for a particular throughput and, therefore, lower capital costs.

We chose the study of rapid hydropyrolysis as a logical extension of our work on catalytic hydropyrolysis. Some rapid heat-up runs, in which nickel carbonate was added, were also included in the study for comparative purposes. The presence of water and the use of cold pressures of 2.07 MPa (300 psig) hydrogen or nitrogen were maintained, again to provide continuity with our previous work. The water also satisfied the requirement for a heat transfer medium. More recent studies show that the reaction is somewhat sensitive to the initial cold pressure, but results are not presented here.

Rapid hydropyrolysis has been studied for cellulose and lignin. Osterman et al (1980) showed that aqueous cellulose, in the absence of sodium carbonate, is liquefied in approximately 10 minutes at 280°C and 310°C with the oil yield (22%, with oxygen content of approximately 20%) being higher at the upper temperature. The heating rate for this study

was about 300°C/minute. For longer residence times the oil yield falls. Bobleter and Concin (1974) have studied the rapid pyrolysis of Willstatter poplar lignin at temperatures of 270-375°C. Their results conformed to an initial depolymerisation of the lignin, probably due to the breaking of ether and related linkages, followed by a slower repolymerisation. The latter process certainly occurs by electrophilic aromatic substitution and involves carbocations, which are generated from the alcohols produced in the initial cleavage. At 365°C, maximum depolymerisation occurred after half a minute, and the repolymerisation process occurred about ten times slower than the rate of depolymerisation. Over 90% of the lignin was soluble in acetone-water mixtures after half a minute. No value was given for the heat-up rate but, from the experimental description of the apparatus and technique, and comparisons with our study, we estimate a rate of 300°C/minute.

EXPERIMENTAL

Apparatus

A tubular reactor made of ½" O.D. 316 stainless steel tubing (0.65" wall thickness), Swagelock Fittings, and a Whitey Union Bonnet valve containing high temperature packing, was used. Its volume was 8 ml. A larger reactor having a volume of 100 ml was also designed. Although some sealing problems were encountered with this vesssel, its major

disadvantage was that it required 8 mins. to bring it to reaction temperature. Experiments were thus confined to the smaller vessel.

The experimental unit, designed to enable rapid heat-up of the reactor, is shown schematically in Figure 1. A Techne fluidised sand bath, SBL-2, was used to heat the vessel. The eccentric drive device, which was used to provide adequate mixing within the reactor, was powered by a Zero Max variable speed motor. It was operated at 430 rpm for all runs in this study.

Technique

The experiments were organised in kinetic series each consisting of six individual runs at residence times of 0, 1, 3, 5, 10, and 20 mins. Non-catalytic runs, and catalytic runs using nickel carbonate, were carried out in the presence of either nitrogen or hydrogen.

Lower reaction temperatures of 230-330°C were used in four runs to determine approximately the temperature at which wood begins to liquefy. Heat-up rates for these runs averaged 300°C/min.

Finally, five identical runs were executed to determine the reproducibility and accuracy of the experimental data.

The wood was seven-year old hybrid poplar, Populus X Eurumericana, clone I-45/51. It was dried for twenty-four hours at 65°C under a reduced pressure of 11 to 17 kPa, and ground in a Tyler ball mill to a powder of less than 35 mesh (0.73 mm grid) in size. The oven-dried poplar contained 49 per cent by weight carbon, 6.3 per cent hydrogen, and

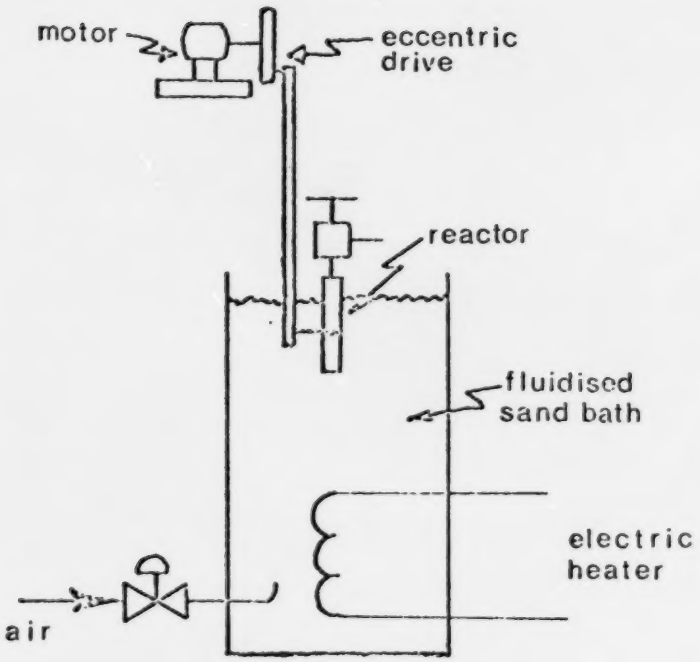

Figure 1: Fast Heat-up Apparatus

44.7 per cent oxygen. The catalyst precursor, nickel carbonate, was a fine, light-green powder. It was manufactured by Matheson Coleman and Bell, and supplied by Canlab.

In a typical run the tube was loaded with 3.3 g distilled water, .77 g wood, 0.15 g $NiCO_3$ (both measured to four significant figures), and 21.07 MPa (300 psig) hydrogen or nitrogen cold pressure. The reactor was attached to the eccentric drive, and the sand bath was preheated to temperatures slightly above the desired reaction temperature of 350°C. The motor was turned on, and the bath was elevated by a manually-operated counterbalanced lift so as to completely immerse the reactor in sand. The reaction was terminated by lowering the sand bath to clear the reactor and moving the lift along the floor rails to bring the cold water bath under the reactor.

The heat-up time for each run was measured as the time from the immersion of the reactor in the sand bath to the time when the sand bath temperature, measured with a thermocouple, reached steady state at 350 ± 5°C. The residence time for each run was defined as the time beginning from when the steady state reaction temperature was reached. For a residence time of 0 min. the reactor was removed from the sand bath as soon as temperature was reached, about 70 to 90 s after it was immersed in the sand.

After the run the gas was vented, and the aqueous phase was poured into a test tube and centrifuged for ten minutes. The oil and solids were removed from the reactor by washing with residue-free acetone. Oil

and solids that were suspended in the aqueous phase were recovered by washing the test tube with acetone after the centrifuged water had been carefully poured off. At this point the acetone contained traces of water that had remained in the reactor and test tube. The acetone wash was then filtered in a 30 ml glass crucible, with a medium frit, to separate out the acetone insoluble phase. The preweighed filter was dried to constant weight in a Fisher vacuum oven at 90 to 95°C under a vacuum of 11 to 17 kPa.

The oil was recovered by evaporating the acetone, and any water contained with it, in a Buchi rotary evaporator for approximately 10 to 15 mins. at 30°C and at reduced pressures of initially 30 to 35 kPa, to remove the acetone, and at 11 to 15 kPa for two minutes to remove the water.

The percentage oil yield was defined as:

$$\text{Oil Yield} = \frac{\text{Mass Acetone Soluble}}{\text{Mass Wood Added}} \times 100$$

Conversion of wood to oil was defined as:

$$\text{Conversion} = \frac{\text{Mass Added} - \text{Mass Acetone Insoluble}}{\text{Mass Wood Added}} \times 100$$

Elemental analysis was performed on the oil products at the Schwarzkopf Micro Analytical Laboratory Inc., 56-19-37th Avenue, Woodside, New York 11377. All samples were dried overnight at 98°C and atmospheric pressure prior to analysis. The percentage by weight of carbon and hydrogen were calculated on an ash free basis, and oxygen content was measured by difference. The carbon and hydrogen mass content in the oil

as a percentage of the feed was calculated from the elemental analysis and oil yield. It was defined as:

$$\%C(C + H) = \frac{(\%C + \%H) \text{ in oil} \times \text{Mass Acetone Soluble}}{(\%C + \%H) \text{ in wood} \times \text{Mass Wood Added}} \times 100$$

RESULTS AND DISCUSSION

In all runs at 350°C, a black oil was produced at the end of the 70 to 90 s heat-up period (time zero). The aqueous phase was gold for runs of short residence time and became darker and green after longer runs. The same colour changes, but over a much longer time period, were observed in catalytic liquefaction work using Raney nickel and slow heat-up to the same temperature, (Boocock and Lee, 1982). All of the oils produced at this temperature flowed at room temperature. Not enough oil was produced in individual runs to conduct viscosity measurements.

Product gases consisted mainly of CO_2 with lesser amounts of CO, C_2H_6, and C_3H_8. The mass of the gases produced could not be determined accurately at the time of these experiments, because these products were present in such small amounts. A system has recently been constructed to handle the quantitative analysis of these gases and preliminary results have been obtained. Details are not included in this paper, but carbon dioxide constitutes 86% of the total gas product.

Because the mass of the gases produced was unknown, and complete separation of the oil and aqueous phases was not achieved, overall mass

balances could not be calculated. To determine the accuracy of the data, five identical runs were executed. The consistency of the data in Table I verifies the reproducibility of the results reported in this paper.

Effect of Residence Time

The production of oil and the absence of unreacted wood for all runs after a time zero (end of 70 to 90 s heat-up period to 350°C), indicates that, under conditions of fast heat-up, the wood is liquefied very rapidly. This liquefaction occurs with and without nickel carbonate in the presence of either hydrogen or nitrogen.

Figure 2 demonstrates that the highest yields were obtained after time zero, and that the oil yield decreased thereafter. This is due to the occurrence of any one or all of the following:

1) Continued cracking of the molecules thus increasing the amount of of gas produced.
2) Oxygen removal from the oil in the form of CO_2, CO, and H_2O.
3) Solids formation through repolymerization reactions that occur simultaneously and compete with the production of molecules of stable liquids.

The effect of residence time on the oxygen content of the oils is shown in Figure 3. After the initial liquefaction period, the oil contains about 25 per cent oxygen whereas the wood contained about 45 per cent. Since carbon and hydrogen make up the balance of both the wood and

the oil, it can be seen that considerably more oxygen than carbon and hydrogen is removed during this period. Over the next 20 min. the oxygen content in the oil decreases from about 25 per cent to 17 per cent, and thereafter oxygen is removed very slowly. This implies that stable oxygen containing molecules, such as phenols and cresols, are produced.

Thus an overall process for producing useful liquids would consist of a rapid liquefaction step to obtain oils at the highest yields, followed by upgrading procedures. The latter could include processes for futher cracking and oxygen removal from the phenolic components.

Table II shows the complete elemental distribution and the higher heating values of the oils. The heating values, which were calculated from Dulong's formula, increase from 28 to 35 MJ/Kg as the oxygen content falls.

The variations in the final pH of the aqueous phase as a function of time is shown in figure 4. From the initial value of 7.8 the pH drops to 2.7-2.9 after time zero. It then increases to 3.6-3.8 within the next 10 to 15 minutes. The lowest pH is due to the formation of carboxylic acids. These acids are then reduced to alcohols or pyrolysed to form carbon dioxide, resulting in the increased pH. A pH of 2.9 is reasonable for carboxylic acids as it can be shown that a 2.7 per cent mass yield of acetic acid would produce this level of acidity. The final pH of 3.6-3.8 is due to the presence of phenolic compounds which are known to be present in the oil (Kallury and Tidwell, 1982).

Comparison of Catalytic and Non-Catalytic Runs

Figure 2 shows that there is a significant difference in the kinetic curves representing oil yield as a function of time for catalytic and non-catalytic runs. The initial yields are lower for the catalytic runs because the presence of nickel carbonate speeds up cracking processes which favour the production of gases and/or water soluble molecules. Char formation, which could not be measured in the presence of nickel carbonate, may also contribute to the lower oil yields. It is significant that the initial carbon, hydrogen and oxygen contents of the catalytic and non-catalytic oils are similar (Table II). Thus in the two cracking processes, the carbon, hydrogen and oxygen are eliminated in the same atomic ratios, indicating that similar reactions are occurring.

Figure 5, which gives the per cent of carbon and hydrogen in the wood that is retained in the oil, shows that at time zero, with no catalyst, 72 per cent is retained in the oil compared to 54 per cent when nickel carbonate is employed. Thus the addition of nickel carbonate is deleterious to the liquefaction process under rapid heat-up.

In the presence of nickel carbonate the oil yields and compositions are the same in both hydrogen and nitrogen atmospheres. If one common species is responsible for this it may well be nickel oxide. Pyrolysis of the carbonate may proceed faster than reduction of the nickel ion in the presence of hydrogen, and once formed, the oxide would be resistant to reduction since it would be insoluble. The inorganic residues from the reaction have not been analysed. Recent work has shown that the

aqueous nickel carbonate does yield the correct quantitative amount of carbon dioxide when heated to 350°C in the nitrogen atmosphere.

Graph of Results

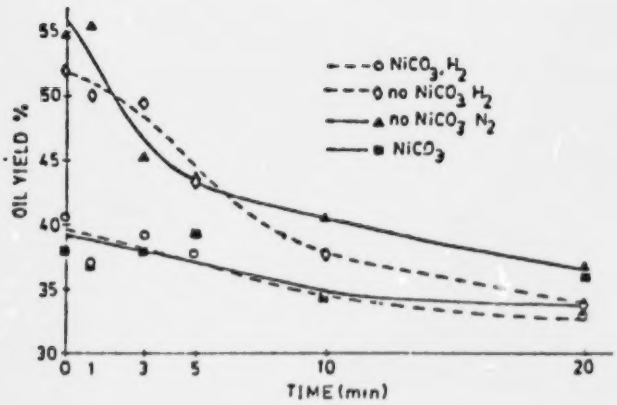

Figure 2: Oil Yields as a Function of Reaction Time

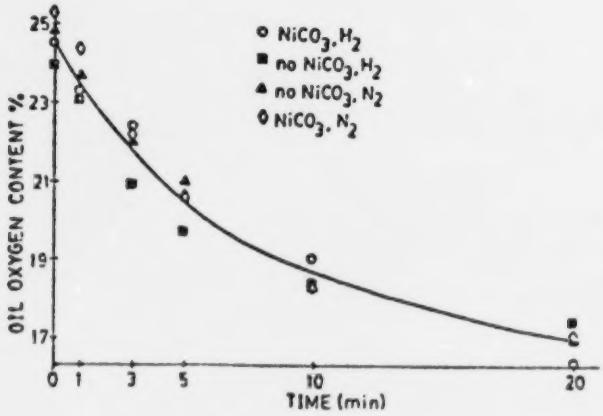

Figure 3: Oil Oxygen Content as a Function of Reaction Time

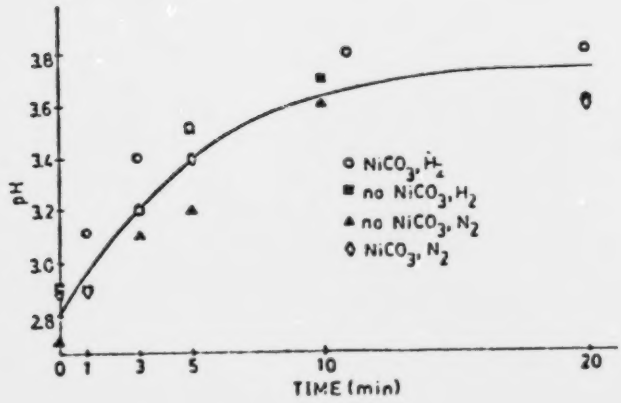

Figure 4: pH of Aqueous Phase as a Function of Time

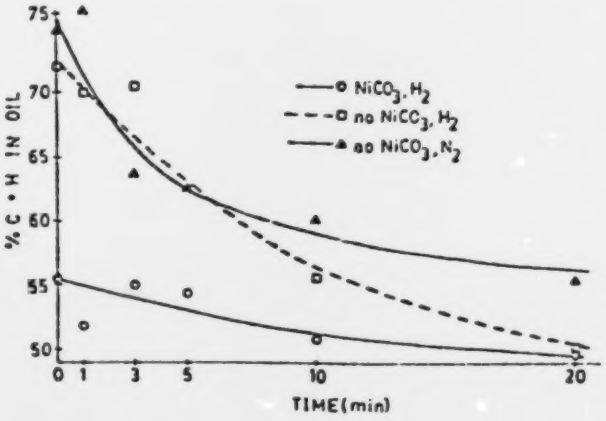

Figure 5: Percentage of Wood Carbon and Hydrogen Retained in Oil as a Function of Time

Hydrogen/Carbon Weight Ratio in the Product Oil

Table IV lists the hydrogen/carbon weight ratios for some of the oils produced under rapid heat-up, and compares them with both oils previously produced under slow heat-up and other liquid fuels. The wood, unlike most coal, contains a sufficient hydrogen-carbon ratio to satisfy idealised liquefaction (Boocock et al, 1980b) in which unsaturated and aromatic hydrocarbons are formed.

Table IV shows that under fast heat-up, no significant difference exists between the H/C ratio for catalytic and non-catalytic runs in the presence of either hydrogen or nitrogen, and that the H/C ratio is independent of residence time. Therefore, under fast heat-up the extent of carbonization of the substrate is not affected by the residence time, gas phase, or $NiCO_3$ activity.

The H/C ratio for these oils (0.095) is lower than that of the wood feed (0.122) because water is presumably a major by-product together with carbon dioxide.

CONCLUSIONS AND CONTINUING STUDIES

The major conclusion of this study is that poplar wood can be liquefied when it is heated rapidly in water to 350°C and immediately quenched. The oil can contain 75 per cent of the carbon and hydrogen originally in the wood. The oxygen content of the oil is about 25 per

cent under optimum yield conditions, whereas the wood contains about 45 per cent. Thus liquefaction can be achieved under conditions which avoid potential problems involved with catalyst separation. Also, liquefaction can be accomplished without the use of a reducing gas. The rapid conversion has important implications for the size of a commercial plant and the associated capital costs. At present, the results are only valid for wood particles of the size studies. Thus, reseach is underway on the heat transfer characteristics of the system and the effect of wood particle size. The role of water as a chemical reactant and heat transfer medium is part of this study.

In a commercial process recoverd heat would be used to partiallyheat incoming feed. Thus studies are being made f the effect of heating the feed slowly to sub-350°C temperatures, followed by rapid heating to 350°C.

Gas phase quantitative and qualitative analyses of the reactor contents are now being carried out on a routine basis using a recently constructed system. The results confirm that carbon dioxide is by far the predominant gaseous product. These and other results will be reported shortly.

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TABLE I: REPRODUCIBILITY OF DATA

Run	% Oil Yield	% Cov.	Oil Composition % C	% H	% O	pH	Q_h (kJ/g)
R1	52.8	96.8	70.6	6.5	22.9	3.10	29.1
R2	53.6	94.7	70.4	6.2	23.4	3.06	28.5
R3	52.8	96.5	70.1	6.4	23.5	3.08	28.7
R4	50.9	96.6	70.2	6.4	23.4	3.02	28.8
R5	52.3	95.9	70.6	6.4	23.0	3.13	29.0
Average	52.5	96.1	70.4	6.4	23.2	3.08	28.8
Standard Deviation	1.00	0.85	0.23	0.11	0.27	0.04	---

TABLE II: ELEMENTAL DISTRIBUTION AND HEATING VALUE OF OIL PRODUCT

Cat.	Gas	Time (min)	Oil Composition % C	% H	% O	$\frac{(C + H)\ oil}{(C + H)\ wood} \times 100$	Q_h kJ/g
		0	69.0	6.6	24.4	55.6	28.5
		1	70.3	6.7	23.0	51.8	29.3
		3	71.3	6.4	22.3	55.1	29.3
$NiCO_3$	H_2	5	72.7	6.8	20.5	54.5	30.7
		10	74.1	6.9	19.0	50.7	31.6
		20	75.8	7.2	17.0	49.5	33.0
		0	69.9	6.3	23.8	72.0	28.4
		1	70.5	6.5	23.0	70.0	29.0
		3	72.6	6.6	20.8	70.7	30.3
none	H_2	5	73.5	6.9	19.6	63.1	31.3
		10	74.7	6.9	18.4	55.6	31.9
		20	75.6	7.0	17.4	50.0	32.5
		0	68.1	6.5	25.4	51.3	27.8
		1	69.2	6.4	24.4	50.2	28.2
		3	71.2	6.6	22.2	53.5	29.6
$NiCO_3$	N_2	5	72.4	7.0	20.6	56.7	30.9
		10	74.6	7.0	18.3	50.7	32.2
		20	75.6	7.3	17.1	54.0	33.0
		0	68.8	6.4	24.8	74.7	28.0
		1	70.0	6.4	23.6	76.7	28.7
		3	71.3	6.7	22.0	63.8	29.8
none	N_2	5	72.4	6.6	21.0	62.7	30.2
		10	74.9	6.8	19.3	60.2	31.8
		20	75.8	7.2	17.0	55.3	33.0

TABLE III: EFFECT OF LOWER REACTION TEMPERATURE

Time (min)	Temp °C	Cat.	Gas	% Oil Yield	% Conv.	Oil Composition % C	% H	% O	pH	Q_h (kJ/g)
0	327	none	N_2	44.4	97.2	62.7	6.9	30.4	2.9	25.7
0	300	none	N_2	42.9	94.2	62.6	6.6	30.8	2.7	25.1
0	267	$NiCO_3$	H_2	27.0	50	--	--	--	--	--
0	230	$NiCO_3$	H_2	NO OIL PRODUCED						
0	350	none	N_2	54.7	96.5	68.6	6.4	24.8	2.7	28.0
0	350	$NiCO_3$	H_2	40.5	--	69.0	6.6	24.4	2.9	28.5

TABLE IV: HYDROGEN/CARBON WEIGHT RATIOS

Substance	Reaction Conditions	Residence Time (min)	H/C
dried wood	---	---	0.122
Wood Liquefaction Oil Product	Cat.: $NiCO_3$ Gas: H_2	0	0.096
		20	0.095
	Cat.: none Gas: N_2	0	0.090
		20	0.093
	Cat.: $NiCO_3$ Gas: N_2	0	0.095
		20	0.096
	Slow Heat-up (Lee, 1979) Cat.: $NiCO_3$ Gas: H_2	60	0.11
Gasoline	---	---	0.18
Octane	---	---	0.19

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